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Metal-free Catalytic Hydrogenolysis of Silyl Triflates and Halides into Hydrosilanes

Gabriel Durin, Albane Fontaine, Jean-Claude Berthet, Emmanuel Nicolas, Pierre Thuéry and Thibault Cantat*

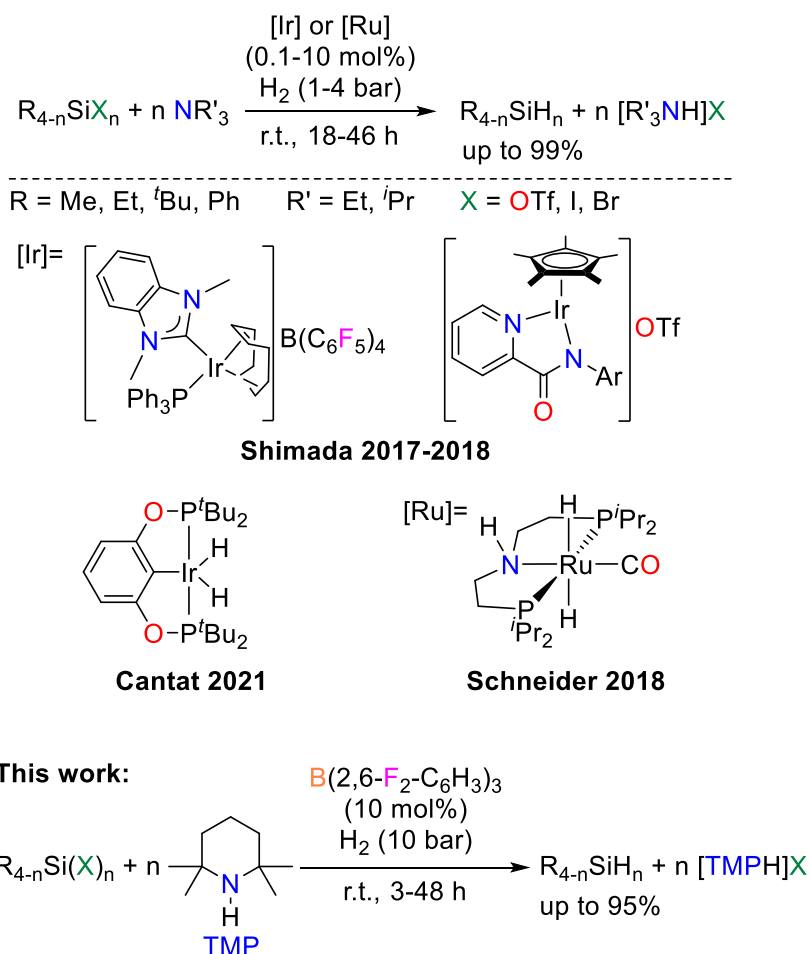
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Abstract

The metal-free catalytic hydrogenolysis of silyl triflates and halides (I, Br) to hydrosilanes is unlocked by using arylborane Lewis acids as catalysts. In the presence of a nitrogen base, the catalyst acts as a Frustrated Lewis Pair (FLP) able to split H₂ and generate a boron hydride intermediate prone to reduce (pseudo)halosilanes. This metal-free organocatalytic system is competitive with metal-based catalysts and enables the formation of a variety of hydrosilanes at r.t. in high yields (>85 %) under a low pressure of H₂ (≤ 10 bar).

Introduction

Hydrosilanes are useful compounds for the production of a variety of organosilicon compounds through hydrosilylation of alkenes or dehydrocoupling reactions.^[1] They also promote, in mild conditions, the reduction of functional groups such as esters^[2] or amides^[3] with high selectivity. In comparison with apolar dihydrogen, the more reductant couple E⁰(Si(OEt)_{4(l)}/SiH_{4(g)} (−0.51 V vs. NHE) and the polarized and weaker Si–H bond (BDE_{Si–H} = 95 kcal.mol^{−1} < BDE_{H–H} = 104 kcal.mol^{−1}) offer some thermodynamic and kinetic advantages^[4] relevant for the reduction of oxygenated chemical feedstocks that will replace oil in the long run (lignin, plastics and CO₂).^[5] Because classical routes for the production of hydrosilanes are energy demanding,^[1b, 6] alternative catalytic syntheses that would transform Si–X (X = halides, alkoxides) precursors into Si–H groups are appealing. This endeavor has motivated the recent elaboration of the first catalytic hydrogenolysis routes to hydrosilanes: in the presence of a suitable base, able to facilitate the thermodynamics of the reaction, Si–X bonds (X = OTf, I, Br, Cl) in halosilanes were successfully reduced to Si–H bonds. Yet, the catalysts reported so far by the groups of Shimada, Schneider and Cantat,^[7] all use catalytic systems based on molecular complexes of noble metals (Ir, Ru) (Scheme 1, top). To improve the sustainability of this reaction and gain fundamental insights into the generation of hydrosilanes, we have sought to unlock the first metal-free catalytic reduction Si–X into Si–H bonds under H₂. Using boranes as catalysts, hydrosilanes (Me₃SiH, Et₃SiH, Ph₃SiH and ⁱPr₂SiH₂) were generated in yields up to 91 %, in the presence of an amine base.



Scheme 1. Examples of catalytic routes that convert silyl halides and triflates into hydrosilanes with H₂ as hydride source.

Mechanistic investigations derived from the iridium and ruthenium catalyzed hydrogenolysis of Si–X bonds have shown that the generation of a metal hydride from H₂ is key to yield a hydrosilane by hydride transfer to the silicon atom.^[7c-e] To perform this deed without a metal, we have sought to use borohydrides as hydrogen transfer reagents. Indeed, borohydrides are known to convert halosilanes into hydrosilanes, as reported by the groups of Klejnot or Nakazawa for instance, who highlighted the stoichiometric reduction of chlorosilanes into hydrosilanes with lithium or sodium borohydride.^[8] Moreover, borohydride species can be generated from H₂ using Frustrated Lewis Pairs (FLP) chemistry as demonstrated by Stephan and others if an appropriate Lewis base is present.^[9] The catalytic hydrogenation of organic functionalities using FLPs has been reported for alkynes,^[10] alkenes,^[11] ketones,^[12] silyl enol ethers,^[13] anilines,^[14] imines,^[15] enamines,^[16] amides,^[17] aza-Morita–Baylis–Hillman adducts,^[18] and esters.^[19] In the case of silyl halides and pseudohalides, a nitrogen base is necessary to be present in stoichiometric amount since the reaction is otherwise endergonic.^[7c-e] Interestingly, the group of Rieger reported on the H₂ cleavage with B/N Frustrated Lewis Pairs (amines and perfluorinated triarylboranes).^[20] The group of O’Hare later demonstrated that the generated borohydride is efficient in the reduction of CO₂.^[21] This result prompted us to consider aryl boranes as catalysts for the hydrogenolysis of Si–X into Si–H bonds, together with stoichiometric amount of nitrogen bases, effectively forming an FLP system in solution.

Using 10 mol% $\text{B}(\text{C}_6\text{F}_5)_3$ and 1.1 equiv. TMP (2,2,6,6-tetramethylpiperidine), only traces of Me_3SiH were obtained from Me_3SiOTf under 10 bar of H_2 at r.t. in CD_2Cl_2 (Table 1, entry 1). The reactivity of a variety of boranes, *i.e.* BPh_3 , $\text{B}(4\text{-F-C}_6\text{H}_4)_3$, $\text{B}(2\text{-F-C}_6\text{H}_4)_3$, $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$ and $\text{HB}(\text{C}_6\text{F}_5)_2$ with distinct Lewis acidities^[22] was thus evaluated. These performances slightly increased with Piers borane^[23] $\text{HB}(\text{C}_6\text{F}_5)_2$ which afforded 21 % NMR yield in Me_3SiH (Table 1, entry 2). In contrast, $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$ and $\text{B}(2\text{-F-C}_6\text{H}_4)_3$ proved quite reactive affording Me_3SiH in excellent yields (88 and 85 % respectively) (Table 1, entries 3 and 4). Compounds BPh_3 and its *para-F* analogue displayed a low efficiency with a poor Me_3SiH yield of 4 % (Table 1, entries 5 and 6). With the most reactive FLP, *i.e.* the TMP/ $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$ couple (Table 1, entry 4), a drop in the Me_3SiH yields was observed either by decreasing the H_2 pressure from 10 to 5 bar (88 to 66 % yield, see ESI Section 2.1.6) or the borane catalyst loading from 10 to 5 mol% (67 % yield, see ESI Section 2.1.7). The results represent the first examples of a metal-free hydrogenolysis of a (pseudo)halosilanes.

Table 1. Screening of borane catalysts for the hydrogenolysis of Me_3SiOTf .^[a]

$$\text{Me}_3\text{SiOTf} + \text{TMP} \xrightarrow[\text{CD}_2\text{Cl}_2, \text{ r.t., 24 h}]{\text{cat. (10 mol\%)} \text{ H}_2 (10 \text{ bar})} \text{Me}_3\text{SiH} + [\text{TMPH}]\text{OTf}$$

Entry	Borane	Computed hydricity ^[24] [kcal.mol ⁻¹]	Conv. ^[b] [%]	Yield (Select.) ^[b] [%]
1	$\text{B}(\text{C}_6\text{F}_5)_3$	65	<1	traces
2	$\text{HB}(\text{C}_6\text{F}_5)_2$	61	21	21 (99)
3	$\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$	51	95	88 (92)
4	$\text{B}(2\text{-F-C}_6\text{H}_4)_3$	48 ^[c]	96	85 (88)
5	$\text{B}(4\text{-F-C}_6\text{H}_4)_3$	37	4	4 (99)
6	BPh_3	36	5	4 (80)

^[a] General conditions: Me_3SiOTf (0.1 mmol), TMP (0.11 mmol), borane (10 μmol), CD_2Cl_2 (0.5 mL), H_2 (10 bar), 25 °C. ^[b]Conversions, selectivities, and yields were determined through integration of the $\text{Me}_3\text{Si-}$ signals by ^1H NMR versus an internal standard (1,3,5-trimethylbenzene). ^[c]This value was calculated for this work.

The NMR yields in Me_3SiH were plotted against the hydricity of the different borane catalysts, that corresponds to the energy required to release a hydride ion H^- from a putative borohydride $[\text{R}_3\text{BH}]^-$ (Figure 1). B–H hydricity values can be obtained from the hydricity scale computed by Heiden *et al.* for main group hydrides;^[24] they quantify the stability of the borohydrides and help appreciating their reducing power. Figure 1 highlights a volcano-type distribution similar to those resulting from the Sabatier principle for heterogeneous catalysts.^[25] It reveals that borohydrides having the lowest hydricities such as $[\text{HBPh}_3]^-$ (36 kcal.mol⁻¹) or the highest such as $[\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2]^-$ and $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (61 and 65 kcal.mol⁻¹) afford poor yields in hydrosilane. This plot likely reveals that a balance must be achieved for an efficient catalytic turnover, where the borane is acidic enough to yield a borohydride from the activation of H_2 , yet able to transfer a hydride ligand to silicon in a subsequent step.

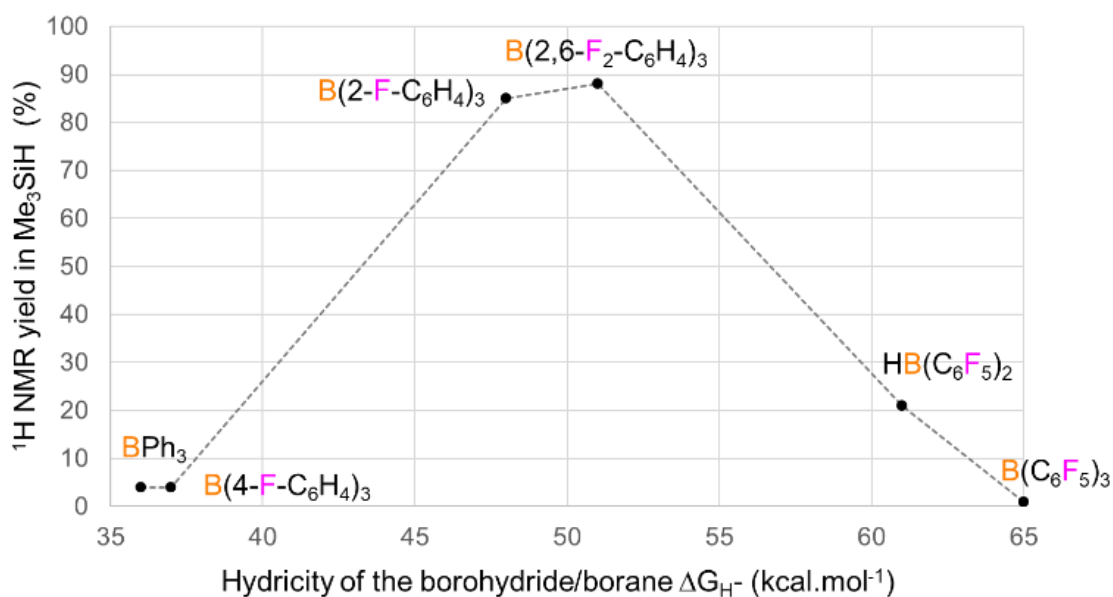
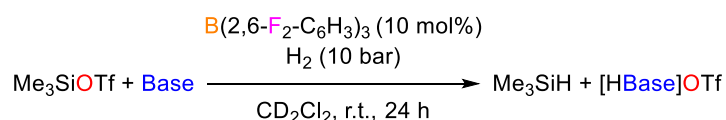


Figure 1. Volcano plot with NMR yield, obtained from Table 2, plotted against the hydricity^[24] of the different arylborane catalysts.

Table 2. Screening of bases for the hydrogenolysis of Me₃SiOTf in CD₂Cl₂.^[a]



Entry	Base	pKa ^[b]	Conv. ^[c] [%]	Yield (Select.) ^[c] [%]
1	2,6-lutidine	14.1	22	15 (68)
2	<i>i</i> Pr ₂ NEt	18.1	48	18 (38)
3	NEt ₃	18.8	82	55 (67)
4	TMP	18.6	95	88 (92)
5	PMP	18.2	39	24 (62)

^[a] General conditions: Me₃SiOTf (0.1 mmol), base (0.11 mmol), B(2,6-F₂-C₆H₃)₃ (10 μmol), CD₂Cl₂ (0.5 mL), H₂ (10 bar), 25 °C ^[b]pKa in MeCN. ^[26] ^[c]Conversions, selectivities, and yields were determined by ¹H NMR spectroscopy, through integration of the Me₃Si signals versus an internal standard (1,3,5-trimethylbenzene).

The role of the nitrogen base was then evaluated by considering a variety of classical and sterically congested amines,^[21, 27] e.g. 2,6-lutidine, trialkylamines NEt₃ and *i*Pr₂NEt, and piperidines (TMP and PMP= 1,2,2,6,6-pentamethylpiperidine) in the conditions depicted in Table 2. With 2,6-lutidine, the reaction led after 24 h at room temperature to the formation of Me₃SiH in 15 % yield (Table 2, entry 1). Replacing 2,6-lutidine with trialkylamines NEt₃ or *i*Pr₂NEt increased the spectroscopic yield in Me₃SiH (18 and 55 %, respectively) (Table 2, entries 2 and 3). This yield reached 88 % with bulky piperidine TMP (Table 2, entry 4 or Table 1, entry 3) but dropped to 24 % with the N-methylated derivative of TMP (1,2,2,6,6-pentamethylpiperidine, PMP), thus underlining a possible influence of the NH group (Table 2, entry 5). A plausible explanation for such a behavior might be the presence of hydrogen bonding N–H•••F interactions between the secondary amine and the fluorine atoms on the triarylborane,

reminding of the adduct described by Bourissou *et al.*,^[28] that pre-organize the FLP for a better activation of H₂ and overall, a more favorable catalytic process.^[29]

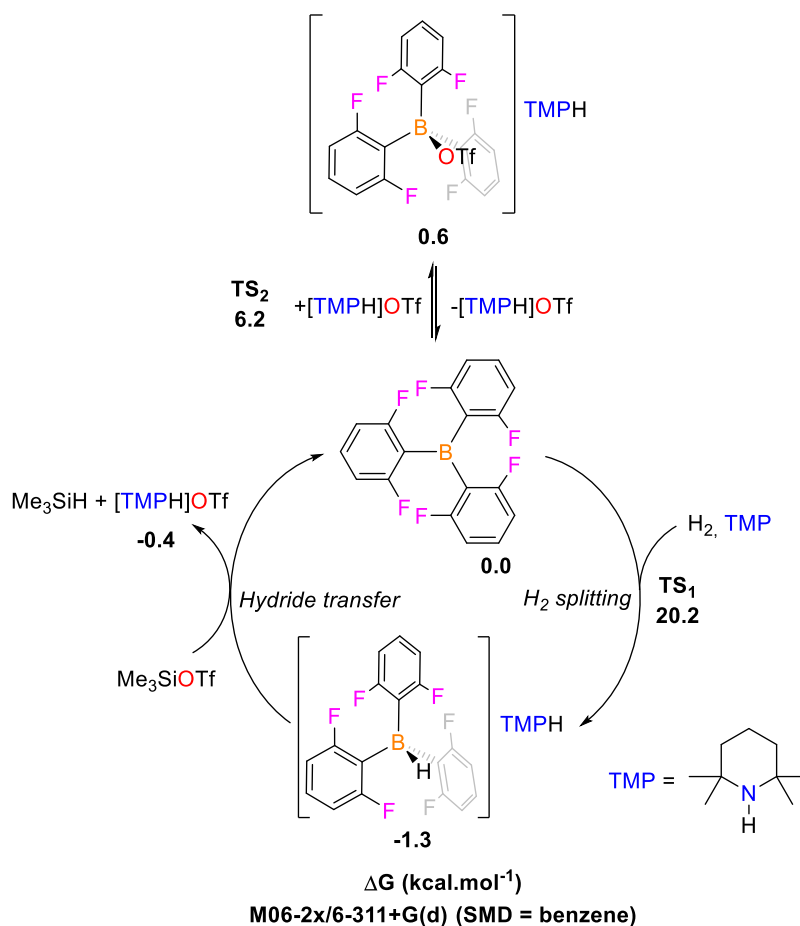
The most productive bases have a pK_a greater than 18, while 2,6-lutidine (pK_a = 14) afforded the lowest yield in Me₃SiH. Nonetheless, as noted previously with transition metal catalysts,^[7d] the Brønsted basicity is not the sole parameter influencing the reactivity of the nitrogen base: NEt₃ and ⁱPr₂NEt are readily trapped by Me₃SiOTf to form the silylated ammonium salts [R₃NSiMe₃][OTf], which has a decreased reactivity compared to the free silyl triflate. These silylated ammonium salts were, in contrast, not observed with the piperidines for which the hydrogenolysis proceeded in CD₂Cl₂ with gradual deposition of the insoluble [TMPH][OTf] or partially soluble [PMPH][OTf] salts (Table 2, entries 4 and 5). When performed with stirring, the reaction proved to be faster in benzene than in dichloromethane, and 3 h instead of 24 h were required to reach the same yield in Me₃SiH (91 %), with TMP/B(2,6-F₂-C₆H₃)₃ (ESI, Section 2.1.5).

The applicability of this catalytic route using these optimized conditions was evaluated with a series of silyl triflates and halides (Table 3). Similar to Me₃SiOTf, Et₃SiOTf is almost fully converted into Et₃SiH (90 %) with an excellent selectivity within 3 h (Table 3, entries 1 and 2). Formation of the bulky Ph₃SiH is much slower and required 48 h to reach 88 % yield from Ph₃SiOTf (Table 3, entry 3). The double hydrogenolysis of the bis triflate ⁱPr₂Si(OTf)₂ is twice as fast as the hydrogenolysis of Ph₃SiOTf and provides ⁱPr₂SiH₂ in 86% yield (Table 3, entry 4). Attempts to synthesize ⁱPr₂SiH(OTf) by using only 1.1 equivalent of TMP afforded ⁱPr₂SiH₂ as the major product (41 %) with low yields in the desired ⁱPr₂SiH(OTf) (9 %) (Table 3, entry 5). Compared to Me₃SiOTf, the reduction of Me₃SiI and Me₃SiBr is slower requiring 7 h and 16 h, respectively, to reach 88 % and 71 % yields in Me₃SiH (Table 3, entries 6-7). Finally, only traces of hydrosilane could be detected in the hydrogenolysis of Me₃SiCl (Table 3, entry 8). These findings are consistent with the trends obtained using organometallic catalysts for the hydrogenolysis of (pseudo)halosilanes, pointing to a more difficult cleavage of the Si-Cl bond.^[7c, 7e]

The hydrogenolysis of (pseudo)halosilanes is somewhat more efficient using the borane catalyst compared to the known Ir and Ru catalysts, which require prolonged reaction times and higher temperatures. For example, Me₃SiH was obtained in 11 % yield with an iridium amido catalyst from Me₃SiBr and ⁱPr₂NEt, after 48 h at 60 °C.^[7a] In the case of Ru(II) bearing a participative ligand, improved performances are reported: Me₃SiH was obtained in 85 % yield from Me₃SiOTf after 18 h at r.t., with only 1 mol% catalyst loading. These results are close to the 91 % yield obtained after 3 h with 10 mol% loading for the borane-catalyzed reaction (Table 3, entry 1).

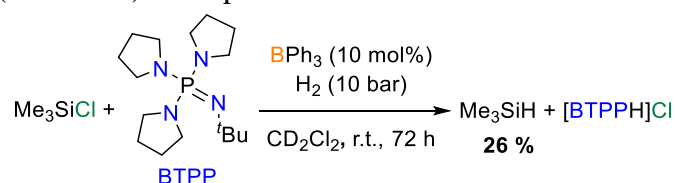
To gain insights into the mechanism of the reaction, stoichiometric experiments have been conducted (Scheme 2). In line with the findings of Paradies *et al.*,^[30] [HB(2,6-F₂-C₆H₃)₃][TMPH] could be generated in near quantitative yield by reacting B(2,6-F₂-C₆H₃)₃ and 1.1 equiv. TMP, under 10 bar of H₂, at r.t. in C₆D₆. Addition of Me₃SiOTf to the latter solution yielded Me₃SiH (93 %) within 5 minutes at r.t., together with B(2,6-F₂-C₆H₃)₃ and a white deposit of [TMPH][OTf].

completion at 10 mol% catalytic loading). A kinetic study based on the time-scale normalization method described by Burés^[31] was performed and revealed a partial order of 1 for the base and 0 for the silyl triflate (see ESI, section 2.3). Such values are in agreement with the DFT calculations and the experiments. A complex order (ca. 0.1) for the borane was also found which shows the detrimental influence of the interaction between $B(2,6-F_2-C_6H_3)_3$ and TfO^- .



Scheme 3. Computed mechanism for the hydrogenolysis of Me_3SiOTf with the FLP ($TMP/B(2,6-F_2-C_6H_3)_3$) (M06-2X/6-311+G(d) level of theory, solvent (benzene) effects are taken into account with SMD).

Capitalizing on this mechanistic knowledge, we next targeted the hydrogenolysis of chlorosilanes, an appealing yet challenging class of substrates.^[7] Regardless of the nature of the base, $B(2,6-F_2-C_6H_3)_3$ proved unproductive in the conversion of Me_3SiCl to Me_3SiH . Nonetheless, as Me_3SiCl has a lower reactivity than Me_3SiOTf , we have considered a mildly acidic borane (BPh_3) in the presence of the strong phosphazene base BTTP (*tert*-butylimino-tri(pyrrolidino)phosphorane) to split H_2 and generate a highly reactive borohydride (hydricity of 36 kcal.mol⁻¹)^[24] (Scheme 4). This particular reaction will be further studied and optimized.



Scheme 4. Hydrogenolysis of Me_3SiCl with the phosphazene BTTP and BPh_3 .

In summary, we have developed an unprecedented transition metal free catalytic route for the hydrogenolysis of silyl triflates and halides (I, Br), using di- and triarylboranes as catalysts. A delicate balance of the Lewis acidity of the borane catalyst is essential for a good activity. In the presence of the base, the catalyst acts as a B/N FLP and the combination of B(2,6-F₂-C₆H₃)₃ and TMP proved the most efficient to afford hydrosilanes in high yields at room temperature and under a low pressure (10 bar H₂). Experimental reactions, kinetic data and theoretical calculations support a two steps mechanism with a rate-determining step being the heterolytic splitting of H₂. This results paves the way for new catalytic systems for the sustainable synthesis of hydrosilanes, a necessary step towards a closed silicon cycle.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

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Keywords: Hydrosilane synthesis • Metal-free • hydrogenolysis • Frustrated Lewis pair • H₂ activation • Borohydrides

References

- [1] a) B. Marciniec, in *Hydrosilylation, Vol. 1* (Ed.: B. Marciniec), Springer Netherlands, Dordrecht, **2009**, pp. 159-189; b) L. Rösch, P. John, R. Reitmeier, in *Ullmann's Encyclopedia of Industrial Chemistry* (Eds.: V. C. H. V. G. Wiley, K. Co), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2000**, pp. 637-669.
- [2] a) H. Li, L. C. Misal Castro, J. Zheng, T. Roisnel, V. Dorcet, J. B. Sortais, C. Darcel, *Angew. Chem. Int. Ed.* **2013**, *52*, 8045-8049; b) S. Hosokawa, M. Toya, A. Noda, M. Morita, T. Ogawa, Y. Motoyama, *ChemistrySelect* **2018**, *3*, 2958-2961.
- [3] S. Das, D. Addis, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770-1771.
- [4] C. Chauvier, T. Cantat, *ACS Catal.* **2017**, *7*, 2107-2115.
- [5] a) E. Feghali, T. Cantat, *ChemSusChem* **2015**, *8*, 980-984; b) L. Monsigny, E. Feghali, J.-C. Berthet, T. Cantat, *Green Chem.* **2018**, *20*, 1981-1986; c) M. Rauch, Z. Strater, G. Parkin, *J. Am. Chem. Soc.* **2019**, *141*, 17754-17762.
- [6] W. Kalchauer, B. Pachaly, in *Handbook of Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, **2008**, p. 2635_2647.
- [7] a) D. Tsushima, M. Igarashi, K. Sato, S. Shimada, *Chem. Lett.* **2017**, *46*, 1532-1534; b) T. Beppu, K. Sakamoto, Y. Nakajima, K. Matsumoto, K. Sato, S. Shimada, *J. Organomet. Chem.* **2018**, *869*, 75-80; c) A. Gluer, J. I. Schweizer, U. S. Karaca, C. Wurtele, M. Diefenbach, M. C. Holthausen, S. Schneider, *Inorg. Chem.* **2018**, *57*, 13822-13828; d) G. Durin, J.-C. Berthet, E. Nicolas, P. Thuéry, T. Cantat, *Organometallics* **2021**; e) G. Durin, J. C. Berthet, E. Nicolas, T. Cantat, *ACS Catal.* **2021**, *11*, 10855-10861.

- [8] a) O. J. Klejnot, *Inorg. Chem.* **1963**, *2*, 825-826; b) M. Ito, M. Itazaki, T. Abe, H. Nakazawa, *Chem. Lett.* **2016**, *45*, 1434-1436.
- [9] a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124-1126; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46-76; c) J. Paradies, *Eur. J. Org. Chem.* **2019**, *2019*, 283-294; d) L. Liu, B. Lukose, P. Jaque, B. Ensing, *Green Energy Environ.* **2019**, *4*, 20-28.
- [10] K. Chernichenko, A. Madarasz, I. Papai, M. Nieger, M. Leskela, T. Repo, *Nature Chem.* **2013**, *5*, 718-723.
- [11] L. Greb, P. Ona-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164-10168.
- [12] T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809-15812.
- [13] H. Wang, R. Frohlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966-5968.
- [14] T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 4088-4091.
- [15] P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050-8053.
- [16] P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Frohlich, G. Erker, *Angew. Chem. Int. Ed.* **2008**, *47*, 7543-7546.
- [17] N. A. Sitte, M. Bursch, S. Grimme, J. Paradies, *J. Am. Chem. Soc.* **2019**, *141*, 159-162.
- [18] I. Khan, M. Manzotti, G. J. Tizzard, S. J. Coles, R. L. Melen, L. C. Morrill, *ACS Catal.* **2017**, *7*, 7748-7752.
- [19] J. S. Sapsford, D. Csokas, R. C. Turnell-Ritson, L. A. Parkin, A. D. Crawford, I. Papai, A. E. Ashley, *ACS Catal.* **2021**, *11*, 9143-9150.
- [20] V. Sumerin, F. Schulz, M. Nieger, M. Leskela, T. Repo, B. Rieger, *Angew. Chem. Int. Ed.* **2008**, *47*, 6001-6003.
- [21] A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839-9843.
- [22] I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.* **2014**, *270*, 75-88.
- [23] D. J. Parks, R. E. V. H. Spence, W. E. Piers, *Angewandte Chemie-International Edition in English* **1995**, *34*, 809-811.
- [24] Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818-1827.
- [25] a) P. Sabatier, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1984-2001; b) M. D. Wodrich, B. Sawatlon, M. Busch, C. Corminboeuf, *ChemCatChem* **2018**, *10*, 1586-1591.
- [26] a) I. Kaljurand, A. Kutt, L. Soovali, T. Rodima, V. Maemets, I. Leito, I. A. Koppel, *J. Org. Chem.* **2005**, *70*, 1019-1028; b) A. M. Kelly-Rowley, V. M. Lynch, E. V. Anslyn, *J. Am. Chem. Soc.* **2002**, *117*, 3438-3447; c) pKa value of TMP taken from the supplier Merck, <https://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/chemfiles/chemfile-2001-2003/vol-3-no-1/traditional-strong-and-hindered-bases.html>, Accessed 07/01/2022
- [27] a) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476-3477; b) C. Jiang, O. Blacque, T. Fox, H. Berke, *Dalton Trans.* **2011**, *40*, 1091-1097.
- [28] S. Moebis-Sanchez, N. Saffon, G. Bouhadir, L. Maron, D. Bourissou, *Dalton Trans.* **2010**, *39*, 4417-4420.
- [29] a) S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 1402-1405; b) T. A. Rokob, I. Pápai, in *Frustrated Lewis Pairs I, Vol. 332* (Eds.: G. Erker, D. W.

Stephan), Springer Berlin Heidelberg, Berlin, Heidelberg, **2013**, pp. 157-211; c) G. Skara, F. De Vleeschouwer, P. Geerlings, F. De Proft, B. Pinter, *Sci Rep.* **2017**, *7*, 16024.

[30] L. Greb, C. G. Daniliuc, K. Bergander, J. Paradies, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876-5879.

[31] a) J. Bures, *Angew. Chem. Int. Ed.* **2016**, *55*, 2028-2031; b) J. Bures, *Angew. Chem. Int. Ed.* **2016**, *55*, 16084-16087.